

GEOCHEMISTRY

Project title: Water Chemistry and Its Relationship to Local Geology: A Yellowstone Case Study

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Objective: This study is an ongoing component of Geology 329 taught from the Indiana University Geologic Field Station, Cardwell, MT. During the field-based class, undergraduate students involved with several environmentally oriented programs (chemistry, biology, ecology, geology, and environmental science) on campus, are involved in their first intensive field experience.

The objectives of the Yellowstone study are two-fold. First, the Yellowstone National Park field trip is a unique opportunity to look at an ecosystem that is heavily influenced by hydrothermal activity, which is in stark contrast to the riparian and mountain systems found in study areas of the Tobacco Root Mountains. During the weeks preceding the Yellowstone trip, the students engage in the collection of field measurements of various aquatic systems encountered in their study areas. This data (including oxidation-reduction potential, pH, temperature, and specific conductance) is used as a comparative set against the data collected in the thermal features of Yellowstone. The range of values encountered in the Yellowstone features gives some extreme values for real world data sets and illustrates how temperature controls many of the other chemical variables and microbial ecosystems.

Secondly, plotting the data on topographic maps gives some notion of the distribution, and the compartmentalization of the thermal features. In addition, the real time data that the students collect and plot is compared to the plots of the field data from the USGS Bulletin 1303 (Rowe et al. 1973) which was collected in the 1960s. The data illustrates the geologically ephemeral nature of the features when compared to time scales of other geologic processes observed and discussed during the course.

Findings: In June 2001, Park Geologist Paul Doss accompanied the group through the Upper Basin at Norris. The group took four sets of field measurements (oxidation-reduction potential, pH, temperature, and specific conductance) at 14 thermal features along the public boardwalk. Over lunch, the data were compiled and plotted on a copy of the figure from Rowe et al. 1973. The data was then compared to the published data from USGS Bulletin 1303 to see which features were new in the last 40 years, which had cooled or were inactive, and where the current hot spots were today.

Later in the afternoon, the group visited Octopus Spring for a look at the controlling factors in the distribution of microbial communities. Groups again took field measurements along the run-

off channel to observe how temperature controls the chemistry and the distribution of the microbial communities. Students plotted their data along their sketched map of the spring and runoff channel. Eight water samples were collected, and H_2S (HS^-), SO_4^{2-} , and Cl^- were trapped with Zn-acetate, BaCl, and AgNO₃ respectively to form precipitates. These were filtered, weighed, and the concentrations of these constituents calculated later at the Field Station. Care was exercised to leave the features as undisturbed as possible, and to avoid reactants making it into the environment.

Project title: Geochemical and Geophysical Investigations of Mine Impacts and the Soda Butte Creek Watershed, Yellowstone National Park

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Objective: The objectives of this project are to examine the geochemical systems of the Soda Butte Creek watershed, and to investigate the impact of mining activities near the Creek's headwaters on stream and sediment chemistry. This is accomplished through: 1) building a long-term database documenting seasonal and annual variations in stream chemistry and metal concentrations in stream waters and sediments, and 2) delineation of shallow subsurface features in the Soda Butte Creek floodplain.

Findings: Sediments and waters of Soda Butte Creek and selected tributaries were sampled twice in 2001. Samples collected in early June represent spring high-flow conditions, while samples collected in early August represent seasonal low-flow conditions. Results of geochemical analysis of samples collected in 2001 are consistent with the pattern established by previous years' findings. Elevated concentrations of metals persist in sediments of Soda Butte Creek immediately downstream of the McLauren tailings deposit. Concentrations of lead, zinc, copper, manganese, silver, cadmium, and iron are elevated in sediments collected in the vicinity of the tailings, and also in sediments near the Republic Creek confluence. However, concentrations decrease rapidly to "background levels" and remain relatively constant within Yellowstone National Park boundaries. Sediment concentrations of silver and cadmium are below analytical detection limits at all sample sites within the Park. By contrast, nickel, manganese, and strontium are depleted in sediments near the tailings relative to downstream sediments. Republic Creek appears to contribute these metals to Soda Butte Creek sediments. Concentrations of nickel in stream sediment diminish steadily downstream, while concentrations of manganese and strontium remain relatively constant downstream of Republic Creek.

Mineralogical analysis of sediment collected in October 2001 was accomplished through x-ray diffraction (XRD). Quartz, plagioclase, calcite, dolomite, smectite, magnetite were indicated in all sediment

samples. Kaolinite and mica were detected in samples representing the upper reach of Soda Butte Creek. Pyrite and hematite were present at irregular intervals in stream sediments. The presence of these iron-bearing minerals was not correlated to the McLauren tailings deposit.

Project title: Dissipation of Thermal and Chemical Disequilibrium in Hot Springs

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Objective: The objective of this study is to determine the kinetics (rates and mechanism) of thermal equilibration and chemical equilibration of hot spring waters as they discharge and interact with the atmosphere. The emphasis is on determining the cooling rate and the rate of gas-water exchange as a function of flow regime. It is hypothesized that the rate of cooling and gas exchange are coupled as both are dependent on the flow regime. If this hypothesis holds then we can develop a model for the rate of gas exchange based on cooling rates, which are far easier to determine than gas exchange rates.

Findings: We focused our study on Ojo Caliente in the River Group. Ojo Caliente is a boiling spring with a very constant chemical composition and a well-developed drainage. At eleven points along the drainage the flow velocities and travel times were determined. In addition we successfully implemented a method to characterize the flow regime (turbulence). This method is based on the rate of dissolution of a gypsum plate. Addressing a concern raised in the review of the permit, it is shown that the water composition in the drainage is not affected by the deployment of the gypsum plates. Water chemistry was also determined along the 11 points. The water cools evaporatively. This is supported by the predictable increase in conservative constituents, such as Na and Cl. The volatile constituents (CO₂, CH₄, H₂S) decrease more or less exponentially with distance from the orifice. This is consistent with degassing models. Interestingly, midway in the drainage we see a sharp increase in cooling and volatile loss. At this point there is more turbulence in the water. This indicates that there might indeed be a correlation between cooling and gas exchange. More work is underway to resolve this.

Project title: Geochemistry, Biochemistry, and Stable Isotope Systematics of Sublacustrine

Hydrothermal Vents in Yellowstone Lake: A Modern Hot Spring Gold-depositing Environment?

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Objective: The objectives of this study are to understand hydrothermal processes in sublacustrine hydrothermal vents in the context of the Yellowstone ecosystem and subaerial hydrothermal systems in and around Yellowstone National Park. In particular, we are using chemical composition, especially minor and trace elements and stable isotopes (H, C, N, O, and S), to understand processes of hydrothermal mineralization and to track potentially toxic and nutrient elements from hydrothermal vents into the micro- and macro-fauna of Yellowstone Lake and the Greater Yellowstone ecosystem. To this end we have sampled lake waters, streams flowing into and out of Yellowstone Lake, sublacustrine sinter deposits and altered sediments, lake and cutthroat trout, bacterial mats and small crustaceans from vent localities, and similar materials from selected subaerial hydrothermal systems Parkwide. In addition, geochemical studies will be carried out on subaerial hydrothermal areas with Ann-Louise Reysenbach and Tina Takacs as part of the NSF-NPS funded microbiological inventory of the Park.

Findings: The geochemistry of Yellowstone Lake is strongly influenced by sublacustrine hydrothermal vent activity. The geothermal source fluid feeding the lake and other subaerial hydrothermal systems can be identified using Cl and hydrogen isotope data on vent samples from Yellowstone Lake and thermal waters at subaerial sites. The chemical composition of sublacustrine hydrothermal vent fluids and the geothermal source fluid indicates strong enrichment of As, B, Cl, CO₂, Ge, Hg, H₂S, K, Li, Mo, Na, Rb, Sb, Si, and W. The Cl concentrations indicate that Yellowstone Lake is about 1% geothermal source fluid and 99% inflowing stream water and that the flux is about 10% of the total geothermal water flux in Yellowstone National Park. With recent swath-sonar mapping studies that show numerous new hydrothermal features, Yellowstone Lake should now be considered one of the most significant geothermal basins in the Park. Hg enrichments in hydrothermal vents and associated fauna contribute to elevated Hg concentrations in lake and cutthroat trout. Enriched Hg in cutthroat has potentially serious implications for grizzly bear, otter, eagle, and osprey populations that feed on cutthroat trout who spawn in the rivers. Hydrothermal deposits occur on the lake bottom near active and presently inactive hydrothermal vents. Centimeter- to decimeter-sized siliceous deposits are cemented and recrystallized diatoms and represent pathways for hydrothermal fluid migration. A second major type of hydrothermal deposit comprises hard, porous siliceous spires that were discovered near Bridge Bay in 1997. At least 8–10 spires up to 7 m tall consist of diatom-rich areas and fibrous masses and globules of amorphous silica that could be microbial in origin. Preliminary U-series dating gives an age of 11 ka for the silica spires. Bridge Bay spires formed in place by growth of chimney-like features from vigorous or long-lived lake-bottom hydrothermal vents. Chemical analyses indicate that siliceous vent deposits are almost always

strongly enriched in As, Ba, Cs, Hg, Pb, and Sr, and are often enriched in Fe, Mo, Mn, Nb, Rb, Ta, Th, Tl, and W relative to normal Yellowstone Lake sediments. Oxygen isotope analyses of silica deposits indicate formation at temperature between 80°C and 160°C. Chemical reaction modeling indicates that amorphous silica saturated fluid that vents into bottom waters at temperatures above 145°C can precipitate amorphous silica by mixing with cold, dilute lake waters.

Project title: Arsenic Biogeochemistry in Yellowstone National Park

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Objective: 1) Determine microbially mediated rates of As(III) oxidation in acid-sulfate-chloride springs in YNP, with special focus on Norris Basin, Lower Geyser Basin and Amphitheater Springs. 2) Evaluate the diversity and nature of chemolithoautotrophic microorganisms inhabiting acid-sulfate-chloride springs of YNP. 3) Characterize relationships among As, S and Fe aqueous geochemistry, solid phase formation and the microbial populations that inhabit the geothermal environments. 4) Evaluate whether microbial populations present in acid-sulfate-chloride thermal springs possess As detoxification strategies that allow survival in these extreme environments.

Findings: Geothermal springs within Yellowstone National Park (YNP) often contain arsenic (As) at concentrations of 10 to 100 μ M, levels which are considered toxic to many organisms. Arsenite (As[III]) is often the predominant valence state at the point of discharge, but is rapidly oxidized to arsenate (As[V]) during transport in shallow surface water. The thermal spring selected for this study (44°43'54.8"N 110°42'39.9"W, Spring No. NHSP106, thermal inventory of YNP) is typical of many springs found in the Hundred Springs Plain of Norris Geyser Basin. The spring was selected after preliminary analyses in October 1999 that showed rapid oxidation of As(III) upon discharge. This spring discharges water between 58°C and 63°C (observed over a one-year period), and exhibits a distinctive sequence of well-separated microbial mats covering the spring floor in both longitudinal and lateral directions. The current study was designed to establish rates and possible mechanisms of As(III) oxidation, and to characterize the geochemical environment associated with predominant microbial populations in a representative acid-sulfate-chloride (pH = 3.1) thermal (58–62°C) spring in Norris Basin, YNP. At the spring origin, total soluble As was predominantly As(III) at concentrations of 33 μ M. No oxidation of As(III) was detected over the first 2.7 m downstream from the spring source, corresponding to an area dominated by a yellow filamentous elemental S-rich microbial mat. However, rapid oxidation of As(III) to As(V) was observed between 2.7 and 5.6 m, corresponding to termination of the S-rich mats, decreases in dissolved sulfide, and commencement of a brown Fe/As-rich mat. Rates of As(III) oxidation were estimated

yielding an apparent first-order rate constant of 1.2 min^{-1} (half-life = 0.58 min). The oxidation of As(III) was shown to require live organisms present just prior to and within the Fe/As-rich mat. Complimentary analytical tools used to characterize the solid phase associated with the brown mat revealed an As:Fe molar ratio of 0.7 and suggested that this filamentous microbial mat contains Fe(III)-oxyhydroxide coprecipitated with As(V). Results from the current work are the first to provide a comprehensive characterization of microbially-mediated As(III) oxidation and the geochemical environments associated with microbial mats in acid-sulfate-chloride springs of YNP.

Detailed molecular characterization of 16S rDNA sequences was also performed on the predominant geochemical zones of the representative acid-sulfate-chloride spring. Analysis of amplified 16S rDNA fragments with denaturing gradient gel electrophoreses (DGGE) confirmed the presence of different bacterial and archaeal populations in each of the primary geochemical zones. Phylogenetic analyses of 1,400 base pair 16S rDNA sequences of clone libraries obtained from the yellow and brown mats suggested that *Hydrogenobacter*-like and *Desulfurella*-like populations dominate the yellow and brown mat communities but that *Meiothermus*-like and *Acidimicrobium*-like populations may also be important as well as numerous archaeal populations present in the brown mat. The appearance of archaeal sequences coincided with the onset of As(III) oxidation and the sequences obtained were affiliated with both Crenarchaeota and Euryarchaeota. The majority of archaeal sequences were most similar to sequences obtained from marine hydrothermal vents and other acidic hot springs, although the level of similarity was generally less than 90%. The role of specific bacterial and archaeal populations regarding oxidation of S, Fe and As is the subject of our continuing effort to understand linkages among microbial populations and geochemical processes in acid-sulfate-chloride geothermal springs. Specifically, we are currently addressing isolation of *Hydrogenobacter*-like populations and Fe(II)-oxidizing populations that may also play a role in As cycling, and that may possess unique As detoxification strategies.

Project title: Sulfur Speciation and Redox Processes in Mineral Springs and Their Drainages

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Objective: The prime objective is to determine the fate of geothermal H₂S from hot springs and geysers. The hypothesis is that H₂S can undergo both oxidation and volatilization. The amount oxidized and remaining in solution will be determined by analyzing the waters for thiosulfate, polythionates, sulfite, and sulfate. The remainder would have been volatilized. Sulfoxyanions will be determined using ion chromatography in a mobile chemical laboratory that can be located on or near site. The origin of thiosulfate and its importance to mineral deposit formation will be studied and the rate of thiosulfate formation from H₂S oxidation will be measured in hot spring overflows where possible.

Findings: During 2001 we made 27 new measurements on thiosulfate in hot springs for a total of

more than 120 determinations along with determinations of H₂S, polythionates, sulfite, and sulfate. We have shown that thiosulfate is formed very rapidly from the oxidation of H₂S and that the oxidation usually happens on exposure to the air but it does happen in a few locations in the shallow subsurface. The oxidation rates are 1–2 orders of magnitude faster than found in the lab at 25°C and there is no evidence that thiosulfate is important in complexing metals or mineral deposit formation at Yellowstone.

**Project title: Geochemistry and Geochronology of Eocene Potassic Volcanism
in the Absaroka Volcanic Field**

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Objective: The objectives of this study are to investigate the origin of magmatic rocks in the Eocene Absaroka Volcanic Province and to use this information to better understand the significance of across strike increases in K₂O contents of rocks in the field and possible tectonic settings of the rocks.

Findings: No additional field work was performed in the Park this year and thus there are no additional findings. This project is now completed.

Project title: Geochemical Baselines in the Greater Yellowstone Area, ID, MT, and WY

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Objective: 1) Provide objective, unbiased geochemical baseline data for about 50 chemical elements determined in samples of rock, active stream sediment, water, plants, and animal scat collected from scattered localities throughout Yellowstone National Park and the adjacent U.S. Forest Service lands. 2) Identify the sources, such as hydrothermal features, past mining, and recreation, of anom-

alous concentrations of selected elements. 3) Determine the chemistry of selected elements in the food chain and how these elements may impact the health of wildlife in the Park. 4) Publish raw data and interpretive reports on results.

Findings: About 600 samples of stream sediment, rock, water, and/or animal scat have been collected from widely scattered sites in and around YNP. These samples have been analyzed for as many as 50 elements. In the northeastern part of the Park, weakly anomalous levels of elements related to mineralized rock or to past mining in the Cooke City area have been detected in samples from the Soda Butte Creek drainage basin. These weak anomalies extend to the confluence of Soda Butte Creek with the Lamar River, where sediments from that stream with only background levels of most elements dilute the anomalous concentrations from Soda Butte Creek to background levels. In the fossil (dead) and active hydrothermal areas of the Park studied to date (mainly areas of geysers and hot springs), a common suite of elements is generally present in water and sediment downstream from each area. Concentrations of some elements that are potentially toxic to animals, such as arsenic and fluorine, are significantly elevated in downstream water and sediment. Such elements can be taken up by plants that are consumed by animals. Concentrations of other potentially toxic elements, such as lead and selenium, are very low in the Park and thus are not considered to be a significant health issue. Cesium seems to be the best unique indicator of hydrothermal activity. Analyses of over 100 samples of bison and elk scat show anomalous concentrations of elements associated with hydrothermal features for those animals foraging near such features, indicating that animals foraging in such areas are ingesting significant amounts of elements such as arsenic and fluorine. The toxic effects of fluorine on elk have been documented by others. The effects on animals of ingesting large quantities of many of the elements determined for this study are not known. Data are lacking on the amounts of elements, such as arsenic and molybdenum, that are being retained and accumulated in animal tissue.

Project title: Quantitative Geochemical Modeling of Calcite Precipitation Kinetics at Narrow Gauge Springs, Yellowstone National Park

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Objective: Yellowstone National Park's Mammoth Hot Springs consists of nearly 100 hot springs scattered throughout step-like travertine terraces. The rapid mineral precipitation rates and known evolution history of the travertine deposits make Mammoth Hot Springs an appropriate site to quantitatively compare theoretical models to real-world measurements of calcite deposition.

Although these concepts were applicable to both travertine and sinter deposits, this study focused on calcite deposition. The water chemistry data obtained at Narrow Gauge Springs were geochemically analyzed and compared with theoretical models. Educational objectives of the study were met within the context of Western Kentucky University Geography Course 440G: Geomorphology. While we have studied carbonate mineral geochemistry in a variety of settings, including investigations into karst landscape and aquifer evolution and the deterioration of historic limestone structures in Europe, a key component of this pilot study was to begin to expand our experience to thermal systems.

Findings: Magma-heated bicarbonate-rich water rises to the surface and rapidly deposits calcium carbonate on the Mammoth terraces. Carbon dioxide is released, with partial pressures found to be approximately 1,000 times above the atmospheric background level. The 60-degree Celsius water obtained at the Western Extension of Narrow Gauge Terrace was geochemically analyzed. The water was found to be supersaturated with calcite, indicating a tendency for calcite deposition. Using an empirical calcite precipitation kinetics rate law, the rate of calcite precipitation was estimated to be 31 mm/year for a water sample obtained in August 2001. A yearlong series of photographs indicated that the spring's actual deposition rate was about an order of magnitude higher. The disparity between laboratory models and observed rates can likely be attributed to several factors, including differences in calcite porosity, growth due to biological activity, carbon dioxide out-gassing, and evolutions in the spring's water and depositional patterns.

Project title: Field Trip to Yellowstone National Park, Water Sampling

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Objective: The use of chemical and physical measurements taken in the field and in the laboratory are used to identify and classify geo-thermal features.

Findings: Measurements of simple chemical indicators including pH and total dissolved solids were successfully used in the identification of: Alkaline, Acid Sulfate, and Neutral Chloride geothermal features.

Project title: Student Project to Measure Geochemistry of Thermal Springs

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Objective: To instruct students about the geochemistry of thermal springs in YNP

Findings: On July 27, 2001, students from the University of Georgia conducted *in situ* measurements of temperature, pH, and total dissolved solids (estimated from specific conductivity) for a number of thermal springs at different localities. Below is a listing of the data we obtained, where temperature (T) is reported in degrees Centigrade and total dissolved solids (TDS) is reported in gm/L.

Norris Geyser Basin: Perpetual Hot Spring: T=90; pH=4.7; TDS=1.48. Firecracker Hot Spring: T=53; pH=3.5; TDS=1.09. Pearl Geyser: T=86; pH=8.3; DS=1.3.

Black Pit Spring: T=80; pH=8; TDS=0.31.

White Creek Area: Spindle Geyser: T=96; pH=8.4; TDS=0.85. White Creek: T=50-58; pH=8.12; TDS=0.27. Octopus Spring: T=85; TDS=0.81.

Mammoth Hot Springs: Narrow Gauge Spring: T=63; pH=9.5; TDS=1.32.

**Project title: Arsenic Geochemistry in Yellowstone National Park:
Occurrence, Speciation, and Transformations**

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Objective: The prime objective is to determine the processes that control the concentrations and redox speciation of arsenic in geothermal springs and geysers and their overflows. As(III) and As(V) will be determined routinely and as facilities become available, methylated forms of arsenic, thioarsenites, and arsine gas will be determined. Processes that mobilize arsenic, precipitate arsenic, and oxidize arsenic will be examined. Oxidation rates will be determined where possible and compared to lab rates.

Findings: We have completed 84 As(III/V) determinations during 2001 for a total of 171 determinations since the first measurements. We have found that arsenic is most commonly in the reduced As(III) state at the discharge point of a hot spring but rapidly oxidizes to As(V) within a very short distance of overflow. The fast oxidation rate is catalyzed by microbes and happens over a wide range

of pH, temperature, and composition. Arsenic concentrations reflect both non-reactive behavior (correlate with Cl) and reactive behavior (no correlation with Cl) and the controls are being investigated.

Project title: Dartmouth College Earth Sciences Field Methods

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Objective: This is one segment of the three-month course of Field Methods in Geology and Environmental Studies taught by the faculty of Earth Sciences Department of Dartmouth College. The objective for the Yellowstone segment was to teach students a number of field methods used in glacial geology, fluvial hydrology, and stream geochemistry.

Findings: The part in stream geochemistry involved sampling stream and hot spring waters for analysis of alkalinity, calcium and chloride concentrations. The sampling was designed to examine the effects of bedrock lithology and hot spring input on stream chemistry. We found, as expected that stream water near hot springs was high in alkalinity and chloride. Stream water running over limestone bedrock was high in alkalinity and calcium. Students were able to use simple mixing models to calculate the contribution of hot spring water to various streams inside Yellowstone.

Project title: Geochemistry of Thermal Springs

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Objective: The overall objective of research in Dr. Hinman's group is to identify controls on the chemistry of springs, runoff channels, and groundwater in thermal areas. Specifically, Dr. Hinman's group studies dissolved, particulate and mineral-precipitate composition to understand the chemical, physical, and biological processes that control the chemistry of thermal spring environments.

Work in 2001 focused on two areas: short-term photochemical processes and longer-term ground-water-surface water interactions.

Findings: Photochemical processes: Studies were conducted at four thermal springs—Black Sand Pool, Chocolate Pots, and the Roadside Springs to test the hypothesis that photochemical processes influence and in some cases control the chemistry of biologically important elements. The relationship between reactive oxygen species and iron was examined. Experiments consisted of several distinct parts.

The first part involved monitoring concentrations of several analytes (dissolved oxygen, hydrogen peroxide, sulfide, ferrous and total dissolved iron) as well as pH and temperature in the springs throughout the day (7–8 p.m.). Concurrent with studies in the spring, concentrations of hydrogen peroxide, ferrous and total dissolved iron were monitored in spring water isolated in whirl-pak bags. Sodium fluoride was added to half the bags to bind iron thus preventing iron cycling and possible hydrogen peroxide formation. These studies demonstrated that iron is important for the production of hydrogen peroxide.

The second part involved monitoring hydrogen peroxide decay in spring water. Water samples were collected from the springs and hydrogen peroxide was added. Hydrogen peroxide, sulfide, ferrous and total dissolved iron concentrations were monitored for two hours. Decay rates varied between the springs, probably as a consequence of differences in initial water chemistry.

For the last part of the study, water was collected from each pool. The bag experiments were repeated under controlled conditions. The purpose of these studies was to determine the role of iron and/or sulfide cycling in hydrogen peroxide formation and decay. The Roadside iron spring has the highest iron concentration of the three springs for which the data has been analyzed. There were significant differences in hydrogen peroxide concentrations in the differently pre-treated waters (i.e. unfiltered water, filtered water without fluoride, and filtered water with fluoride). In the filtered water with fluoride, there was no significant hydrogen peroxide formation demonstrating that when iron is in an unreactive form, hydrogen peroxide is not produced. The Roadside sulfur spring and Black Sand Pool both have lower iron concentrations and behaved similarly. There were significant differences in hydrogen peroxide concentrations in the differently pre-treated waters. In the filtered water with fluoride, there was significant hydrogen peroxide formation. However, hydrogen peroxide formation was lower than in the filtered water without fluoride suggesting that more than one pathway results in hydrogen peroxide production.

Hydrogeological and hydrochemical Investigations: Rabbit Creek is lined with a hard mineral deposit along most of its reach. Previous studies on this type of material suggest it forms in losing sections of thermally influenced streams. Rabbit Creek was examined to determine whether this relationship holds and to identify possible biological factors that contribute to the mineral formation. The study of the hydrogeology and hydrochemistry of these mineral deposits involves measurement of discharge, groundwater flow, and water chemistry, as well as characterization of the deposits themselves and the associated biota.

Since August 2001, stream discharge has been constant. Water table has risen less than inch. Stream temperature has dropped 8°C and groundwater temperature has dropped 5°C to 20°C between October and January. The pH of groundwater (7–8), surface water (8–9.5), and hot springs is relatively constant. Anion concentrations (Cl- 200–300mg/L; F- 20–25mg/L; SO₄²⁻ 15–

20mg/L) increased in the winter compared to the summer. Cation concentrations are dominated by Na (>300mg/L), K (10–15mg/L), B (1–3mg/L), and Si is currently precipitating from solution. Alkalinity is in the range of 200–300mg/L CaCO₃. Preliminary interpretation suggests that thermal water becomes more important as a source of recharge to the shallow aquifer during winter months.

Project title: Carbon Dioxide Emissions Related to the Yellowstone Volcanic/Geothermal System

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Objective: 1) To determine the magnitude of CO₂ emissions due to the Yellowstone volcanic/hydrothermal system in the context of other globally important volcanic systems. 2) To monitor background temporal variability of CO₂ emissions due to environmental conditions as a baseline to be compared to changes in emissions due to changes in hydrothermal or seismic activity. 3) To study the spatial distribution of CO₂ emissions and investigate controls on spatial heterogeneity of gas emissions. 4) To monitor gas chemistry including carbon and helium isotopes to gain a broader understanding of the sources of gas emissions and interactions with the hydrothermal system. 5) To test eddy covariance as a new method for measuring emissions in volcanic and hydrothermal terrain.

Findings: Three papers have been published on our work on CO₂ degassing in Yellowstone, and one is in being submitted.

Werner, C. Brantley, S., and Boomer, K., 2000, CO₂ Emissions related to the Yellowstone Volcanic System: 2: Statistical Sampling, Total Degassing, and Transport Mechanisms, *Journal of Geophysical Research*, Vol.105, B5, 10,831–10,846.

Abstract: A stratified adaptive sampling plan was designed to estimate CO₂ degassing in Yellowstone National Park and was applied in the Mud Volcano thermal area. The stratified component of the sampling design focused effort in thermal areas and the adaptive component in high-flux regions, yet neither sampling technique biased the estimate of total degassing. Both diffuse soil fluxes (up to ~30,000 g m⁻² d⁻¹) and emission rates from thermal vents (up to 1.7 x 10⁸ mol yr⁻¹) were measured in thermal areas. Soil fluxes observed in most nonthermal regions were similar to values reported for conifer forests (15 g m⁻² d⁻¹). However, through adaptive sampling, high-flux vegetated sites were identified in Mud Volcano that likely would not have been found if sampling was focused in obvious thermal or altered regions. A simple model applied to flux measurements suggests that ~40% of the analyzed measurements were dominated by possible advective transport and ~30% by diffusive transport. Isotopic signatures of soil CO₂ generally suggest a deep origin

($\delta^{13}\text{C} = -2.3$ to 0.0) in thermal areas and biogenic origin ($\delta^{13}\text{C} = -20.5$) in nonthermal, low-flux areas. Vent emissions accounted for $\sim 32\text{--}63\%$ of the total degassing observed at Mud Volcano (2.4 to 4.0×10^9 mol yr $^{-1}$). The largest source of error in the estimation of total degassing (factor of ~ 2) resulted because the population distribution of thermal feature emissions was indeterminate. Total CO_2 emissions at Mud Volcano are comparable to other hydrothermal regions worldwide, suggesting that the Yellowstone volcanic system is likely a large contributor to global volcanic/metamorphic/hydrothermal (VMH) emissions.

Boomer, K., Werner C., and Brantley, S.L., 2000, CO_2 Emissions related to the Yellowstone Volcanic System: 1: Development of a Stratified Adaptive Cluster Sampling Plan, *Journal of Geophysical Research*, 105, B5, 10,817–10,830. (no abstract)

Werner, C. Wyngaard, J., Brantley, S., 2000, Eddy-Correlation Measurement of Hydrothermal Gases, *Geophysical Research Letters*, Vol. 27, No. 18, 2,925–2,929.

Abstract: In the first application of eddy correlation in a hydrothermal region, we measured turbulent fluxes ranging between -17 and $13,500$ g CO_2 m $^{-2}$ d $^{-1}$ in Yellowstone National Park (YNP). These turbulent fluxes are similar in magnitude to chamber measurements of diffuse fluxes in the region. Negative turbulent fluxes due to vegetative uptake were measured in non-thermal regions. The flux footprint was used to compare turbulent with surface fluxes within the source area of EC measurements, and turbulent fluxes were consistent within error to the spatial extrapolation of chamber measurements. EC is more representative than chamber techniques, providing a viable alternative to measuring gas emissions in volcanic and hydrothermal terrain.

Work in progress: An investigation of the CO_2 fluxes in Upper Geyser Basin, Mammoth Springs, Roaring Mountain, Washburn Springs, Crater Hills, and the Lamar River Valley suggest that diffuse degassing is highest in acid-sulfate and travertine precipitating regions, and lowest in regions of silica precipitation and sulfur flows.